Ceramic Materials and Ceramics Pigments based on high amounts of Industrial and Agricultural wastes

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Introduction

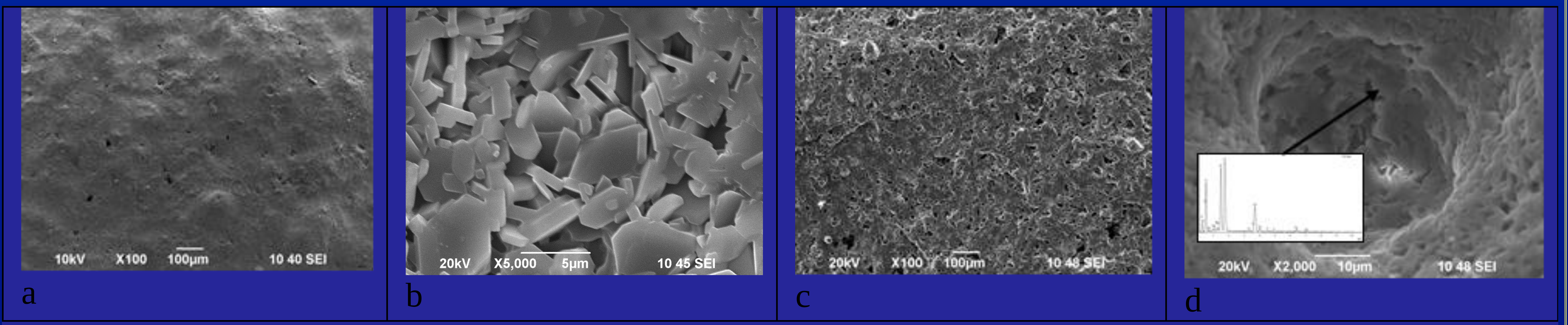
The traditional ceramics are heterogeneous materials, obtained mainly by mixing of three types of natural raw materials (i.e. clays, feldspars and sands). The feldspars are the most expensive raw materials and therefore their replacement can reduce significantly the final costs of ceramics. For this reason, many studies, related to the usage of different alternative fluxing agents, were carried out. Promising results were obtained using soda–lime glass cullet, cathode ray tube of TV or PC monitors and granite cutting sludge.

Other works examine the possibility to use industrial streams as Blast Furnace Slag, MSW ashes, fly ashes from thermal stations and various sludge. Usually, these residues are added as inert materials so that the sintering process is related mainly to the presence of traditional ceramic fluxes. However, if the melting temperatures of used wastes are reached they also start to participate in the formation of the liquid phase, which drastically changes the sintering behavior, the phase composition and the structure of final ceramic. In some cases, this feature gives the exceptional possibility for a total removal of the feldspars. In addition, these innovative ceramics are characterized with higher crystallinity and improved mechanical properties. Here are presented the specific structures of four new ceramics, obtained without traditional fluxes and with high amounts of industrial wastes.

Other interesting trend in the ceramic industry is the usage of different agriculture by-products. Usually, in order to decrease the fuel consumption, these organics residues can be added in the batches for bricks manufacture. However, when their “as it is” combustion is applied for a direct energy production, the resulting ashes also might be used in the ceramic industry. One of the most interesting objects are the rice husks ashes (RHA), which are used in different manufactures, including the synthesize of ceramic pigments.In the present work the possibility to use RHA in new willemite (Zn_2SiO_4) pigments is shown.

Results & Discussion

- The possibility to produce ceramics without feldspars flux is demonstrated with four different compositions. The first ceramic (labelled as CSK-70) was obtained by mixing 70 wt% granulated Blast Furnace Slags (BFS) with 30% kaolin (K), while the second (labelled as CSSK-30) - by mixing 30 % BFS, 40 % quartz sand (S) and 30% K. The other two compositions were prepared using 40% industrial clays and 60% of two different fractions of bottom ashes from Municipal Solid Waste Incinerators (large, L, and fine, F). These ceramics are labelled CLK-60 and CFK-60, respectively.
- The chemical compositions of presented ceramics are very different from the traditional clay-feldspar-sand ceramics. They are characterized with elevated amount of CaO and lower silica percentage as well as with presence of MgO and iron oxides.
- DTA-TG results highlight typical effects of clays and carbonate decompositions followed by exo-effects in the interval 900-1050 ^{o}C due to the formation of anorthite and/or pyroxenes. At 1100-1250 ^{o}C are observed intensive endo-effects of melting of the these newly formed phases, which are diverse from the larger endo-effects with lower intensity in the traditional ceramics.
- The dilatometric sintering curves highlight that rapid densification carries out in the temperature interval of endo-effects; this also is different from the traditional compositions, where the sintering usually is observed at temperatures higher than one of the feldspar melting.
- The XRD results elucidate formation of 40-50 % anorthite solid solutions and pyroxenes, which is untypical for the traditional ceramics, where the main crystal phases are mullite and quartz and the crystallinity is lower.
- The samples demonstrate a good degree of sintering and water absorption values between 0.2 to 1.3 %, which is unusual considering the lower amount of residual amorphous phase. This very positive peculiarity can be explained with the substantial phase formation (at about 10-15 %), taking place during the cooling, which hewer is related with the formation of extra crystallization induced closed porosity.
- The good degree of sintering and the enhanced crystallinity of new ceramics were confirmed with SEM-EDS observations. In Fig. a nonporous surface of ceramics CSK-70 is demonstrated. The image at higher magnification from Fig. b demonstrate the high crystallinity in the surface of CFK. Fig.c shows a fracture of CSSK-30 with mainly closed porosity. Finally, the image from Fig. d presents a typical closed pore in CLK with elevate crystallinity due to phase formation, taking place at the cooling step; EDS spectra confirm the anorthete formation.
- The observed structure explain the exceled mechanical charatersitics of the new material: 40-60 MPa bending strength, 45-50 GPa Young’s modulus and 7.5-8 Mohs hardness.
- The XRD results with the willemite pigments demonstrate some increasing in the rate of formation of final crystal phase when the traditional SiO_2 sources are substituted by the amorphous RHA. In addition, the hot stage microscopy highlight that this replacement leads to an acceleration of the melting of pigments in the high temperature interval 1250-1300 ^{o}C.



SEM images of the studied ceramics

Conclusions

The phase compositions of studied ceramics are different from these of the traditional ones. The main crystal phases, instead quartz and mullite, are anorthite solid solution and pyroxenes. In addition, the amounts of residual vitreous phase are inferior. Notwithstanding the samples are characterized with a negligible open porosity and about 15-20 vol % closed porosity.

In the compositions with lower crystallization trend the pores are spherical and with smooth surface, while in the compositions with higher crystallization trend fine-polycrtalline structure is observed in surface, fracture and pores. This structure is result of a crystallization process, taking place during the cooling. This additional crystallization improves the mechanical properties.

The results with the pigments highlight that the substitution of traditional SiO_2 sources with amorphous RHA accelerates both phase formation and melting processes.

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